# Blends of two poly(aryl ether ketones)

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Miscibility in the amorphous and the crystalline phases of a blend of poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) [poly(ether ether ketone) (PEEK)] and poly(oxy-1,4-phenylenecarbonyl-1,4-phenylene) [poly(ether ketone) (PEK)] has been studied by differential scanning calorimetry (d.s.c.) and wide-angle X-ray diffraction (WAXD). Our results indicate that the polymers cocrystallize on quenching from the melt but do not cocrystallize when other thermal histories are imposed. Conclusions regarding miscibility in the amorphous phase cannot be drawn on the basis of the presence of a single glass transition. However, it can be inferred from results obtained for the crystalline phase that the two polymers are miscible in the amorphous phase.

**(Keywords: blends; poly(ether ether ketone); poly(ether ketone); miscibility; cocrystallization)**

## INTRODUCTION

In the past decade many miscible polymer pairs have been identified, and have been listed in a number of sources[1,2]. Most studies of macromolecular blends have concentrated on amorphous polymers, but some miscible blends in which one or both of the components crystallize have also been characterized[3,4]. However, there are only a few cases known of blends in which the components exhibit isomorphic behaviour[5-8]. For example, in a recent study of blends of poly(aryl ether ketones), it has been suggested that cocrystallization occurs for pairs of polymers in which the difference in the ketone content is less than 25 wt%[9].

Generally, in a binary system cocrystallization is unlikely since it requires close matching of chain conformations and of lattice symmetry and dimensions. Furthermore, both polymers must show some degree of compatibility in the melt and the crystallization kinetics cannot be widely different, as has been discussed by Allegra and Bassi[10], and by Wunderlich[11]. A well known case of reported cocrystallization, the blend of poly(vinyl fluoride) and poly(vinylidene fluoride)[6,8] was subject to criticism in a recent contribution[12].

In this study, blends of two poly(aryl ether ketones), namely poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) [poly(ether ether ketone); PEEK)], and poly(oxy-1,4-phenylenecarbonyl-1,4-phenylene) [poly(ether ketone); (PEK)], described as isomorphous by Harris *et al.*[9], have been characterized. It is the purpose of this report to discuss cocrystallization of PEEK and PEK polymers in these blends. The miscibility of the amorphous phases of the two homopolymers will also be commented upon.

## EXPERIMENTAL

The PEEK and PEK homopolymers were donated by ICI, UK, and Raychem Corporation, respectively. Both materials were used as synthesized and contained no additives. The PEEK homopolymer sample is the same as that used by Bishop *et al.*[13] [PEEK-4] with an intrinsic viscosity $[\eta]$ of 1.124 dl g$^{-1}$ in $H_2SO_4$ at 30°C. The PEK homopolymer had an intrinsic viscosity $[\eta]$ of 1.107 dl g$^{-1}$ in $H_2SO_4$ at 30°C.

Blends of PEEK and PEK of various compositions were prepared by solution coprecipitation. Weighed amounts of both components were dissolved together in dichloroacetic acid (Aldrich Chemical Co.) at a concentration of 1% (w/v). The solutions were heated to $150 \pm 2$°C with stirring under nitrogen, and clear solutions were obtained. The solutions were allowed to cool, and then slowly poured with stirring into a ten-fold excess of a methanol–water mixture (50:50, v/v). The precipitated powder was filtered, washed with methanol and dried in a vacuum oven at 50°C to constant weight. In control experiments, the individual pure polymers were subjected to the same treatment. Physical mixtures of the two polymers were prepared by pouring two separate polymer solutions, in sequence, made as described above into the same methanol–water mixture. The composition of the blends is reported below as weight per cent.

The chemical compositions of both precipitated polymers from the control experiments were determined by elemental analysis. The results are in good agreement with the analysis of the original samples as received, indicating that no apparent chemical modification of the polymers had taken place during dissolution in dichloroacetic acid. Furthermore, the fact that the glass transition temperatures ($T_g$), heat capacity changes at the glass transition ($\Delta C_p$) and the crystalline melting points ($T_m$) of both polymers before and after the acid treatment are identical indicates that the dichloroacetic acid acts merely as a solvent for the polymers.

Thermal analysis was carried out with 10–15 mg samples in a Perkin–Elmer DSC 7 differential scanning microcalorimeter controlled by a Perkin–Elmer 7500 PC. The heating rate was 25°C min$^{-1}$, and the cooling rate was 1°C min$^{-1}$ except as otherwise noted.

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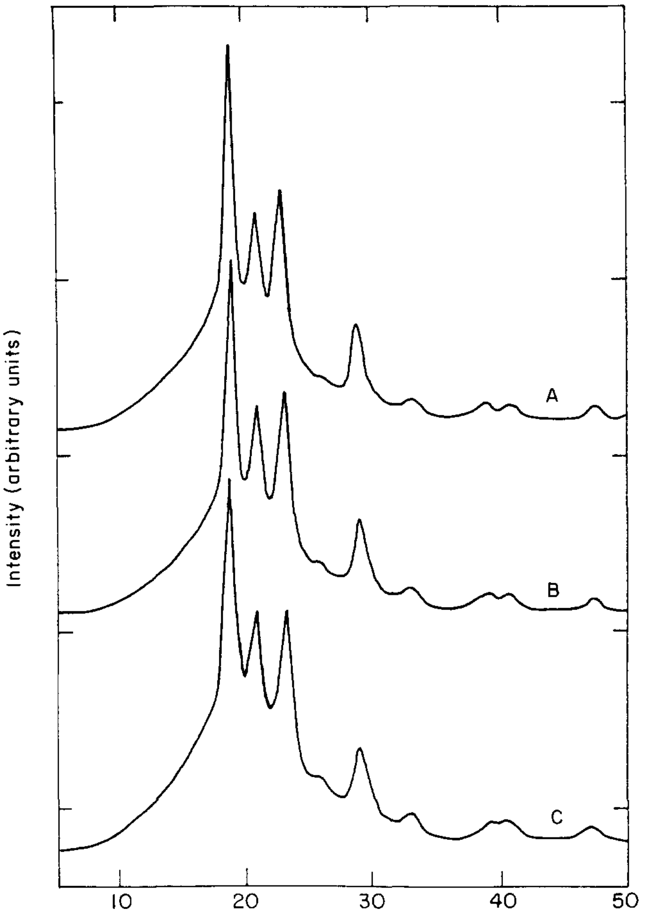

**Figure 1** X-ray diffraction patterns for compression moulded samples from precipitated powders: A, PEEK; B, 50/50 blend; C, PEK

Wide-angle X-ray diffraction (WAXD) scans were measured using a D-500 Siemens diffractometer with nickel-filtered CuK$\alpha$ radiation. The $2\theta$ scan data were collected at 0.02° step intervals in the range of $18° \leqslant 2\theta \leqslant 32°$, and 0.2° steps at other angles. The samples for these measurements were prepared by compression moulding of the coprecipitated powders at 400°C for 5 min followed by slow cooling to room temperature.

## RESULTS AND DISCUSSION

### *Crystalline phase*

The X-ray diffractograms of the two polymers and of the 50/50 wt% polymer blend are shown in *Figure 1*. In agreement with the literature[14], the patterns of the two polymer components are virtually identical; thus it is impossible to distinguish whether the two polymer components cocrystallize or form separate crystalline phases in the blends.

The d.s.c. analysis is more revealing. In fact the difference between the melting temperatures of the two polymers is in the range 25 to 30°C. The melting endotherms for the two polymers and for different blends after precipitation from solution are shown in *Figure 2a*. The crystallization exotherms of the same samples obtained on cooling of the melt at 1°C min$^{-1}$ after being held at 400°C for 5 min are shown in *Figure 2b*. The melting endotherms of samples that had been crystallized at a cooling rate of 1°C min$^{-1}$ are shown in *Figure 2c*. The d.s.c. scans of the blends are generally not characterized by single melting or crystallization peaks but the presence of two superimposed endotherms or exotherms is clearly suggested. The overall heats of fusion are nearly composition independent for the cases of both *Figures 2a* and *2c*.

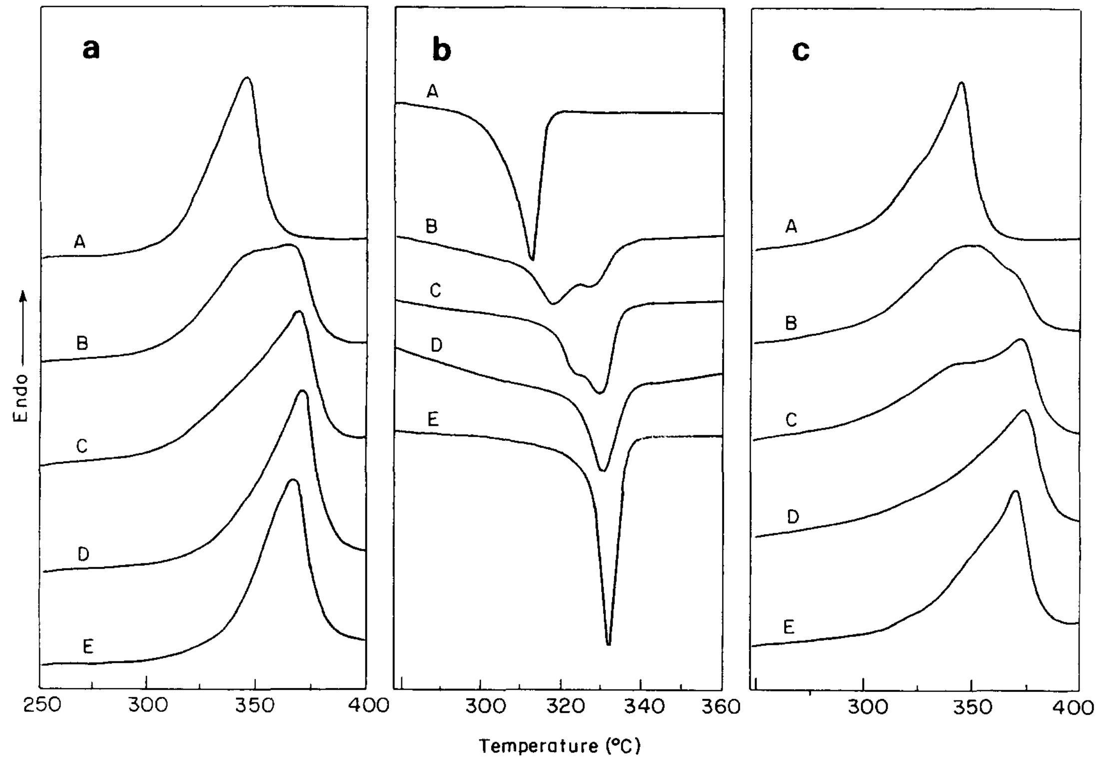

**Figure 2** D.s.c. scans showing the melting of (a) the precipitated powders, (b) the crystallization on cooling at 1°C min$^{-1}$ of samples previously held at 400°C for 5 min, (c) the melting of the samples crystallized on cooling at 1°C min$^{-1}$ for: A, PEEK; B, 75/25 blend; C, 50/50 blend; D, 25/75 blend; E, PEK. In order to facilitate the comparison the ordinate axis is arbitrarily expanded in *Figure 2b*

The shapes of these endotherms are not dependent on heating rate, as shown for the example in *Figure 3* for the first melting of the 75/25 wt% PEEK/PEK blend. Hence, the double peak shape of the melting endotherm is not caused by recrystallization which may occur during the measurement; it actually reflects the melting of two different species. On the other hand, the temperatures of the peaks and the shoulders of the melting endotherms correspond approximately to the crystalline melting temperatures of the two pure polymers, suggesting that no cocrystallization occurs, at least under these conditions.

Isothermal crystallization experiments were also carried out in the range 270–350°C for the 50/50 wt% blend. The samples were first heated to 400°C and held for 5 min and then quenched to the crystallization temperature, $T_c$, and kept for the crystallization time, $t_c$. In all the cases, as shown for instance in *Figure 4* for $T_c = 330$°C, there are two well defined melting peaks whose positions are not far from those measured for the two pure polymers under the same conditions.

The melting endotherms of the two polymers and of some blends quenched from the melt with a cooling rate of approximately 100°C min$^{-1}$ are shown in *Figure 5a*. For the entire composition range, single-peak endotherms are obtained whose heats of fusion are reduced by 30–35% with respect to the melting of the precipitated powders (*Figure 2a*) or of the samples slowly cooled from the melt (*Figure 2c*). The temperatures corresponding to the maxima of these endotherms ($T_m$) are shown as a function of the blend composition in *Figure 5b* and are in good agreement with the data reported in ref. 9. These data seem to confirm that cocrystallization does occur upon quenching from the melt.

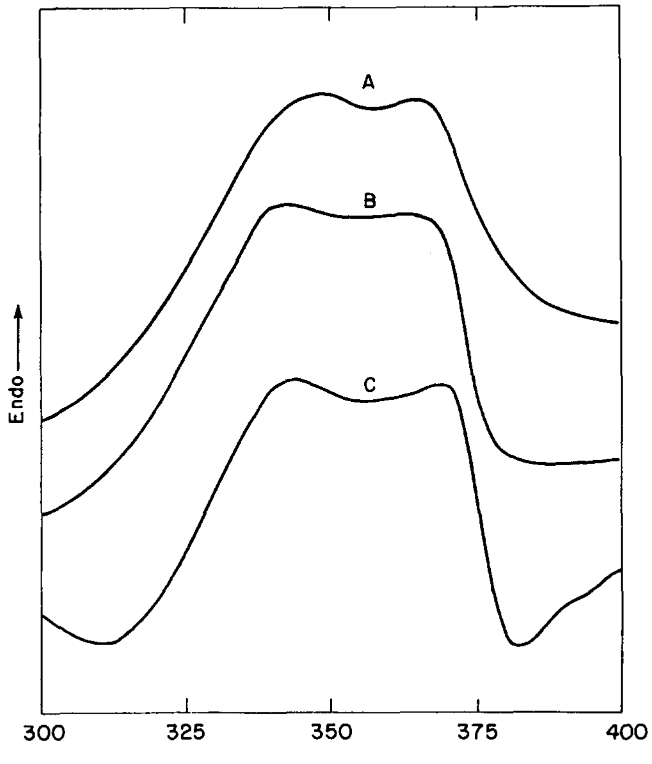

**Figure 3** D.s.c. melting scans for the PEEK/PEK 75/25 blend, as precipitated, at different heating rates: A, 40°C min$^{-1}$; B, 10°C min$^{-1}$; C, 2.5°C min$^{-1}$. In order to facilitate the comparison the ordinate axes are arbitrarily expanded

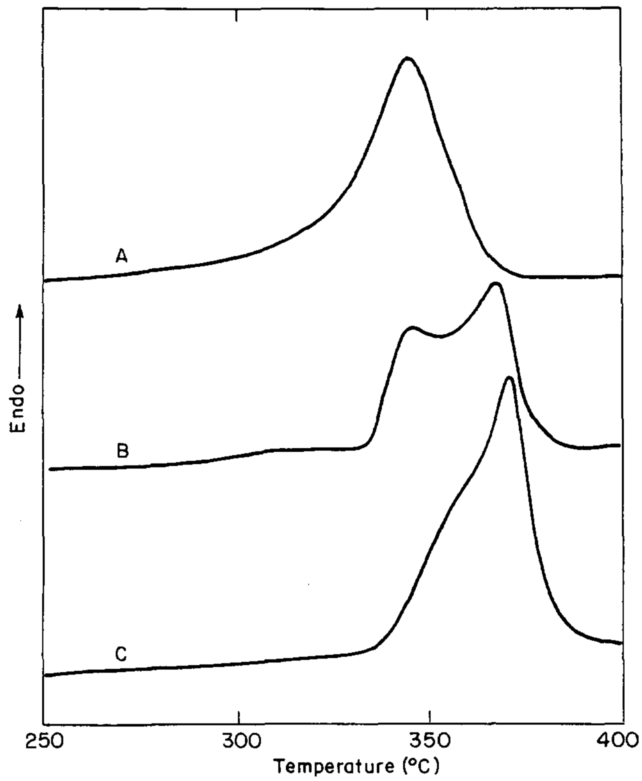

**Figure 4** D.s.c. melting scans of samples isothermally crystallized at 330°C for 2 h: A, PEEK; B, 50/50 blend; C, PEK

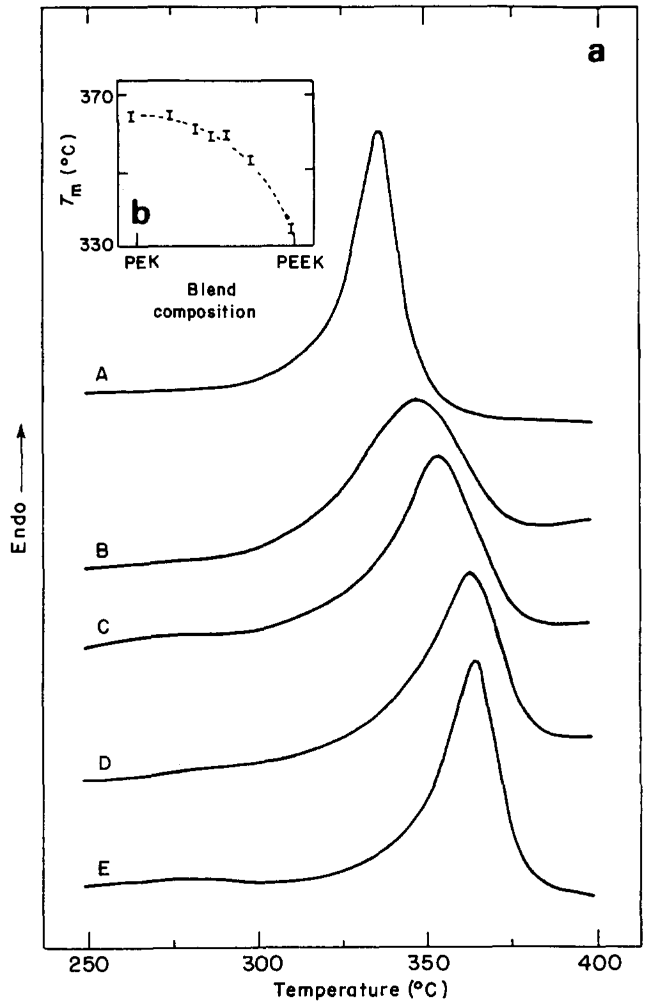

**Figure 5** (a) D.s.c. melting scans of samples quenched from the melt: A, PEEK; B, 75/25 blend; C, 50/50 blend; D, 25/75 blend; E, PEK. (b) Maximum melting points ($T_m$) versus blend composition

Some annealing experiments were also performed. The melting scan of a 50/50 wt% blend annealed for 2 h at 350°C, a temperature intermediate between the melting temperatures of the two pure polymers, for instance is shown in curve B of *Figure 6*. The melting scans of pure PEEK and PEK, subjected to the same thermal treatment, are shown in curves A and C, respectively, of *Figure 6*. The scan of the blend shows a well defined peak with $T_m = 368°C$, which is very close to the peak of PEK ($T_m = 372°C$) and a very broad endotherm at lower temperatures. The measured heat of fusion per gram of the high temperature endotherm is about half the heat of fusion measured for the pure PEK, (compare curves B and C in *Figure 6*). This melting behaviour of the samples annealed at 350°C, is essentially independent of the previous thermal history, and in fact holds for precipitated, slowly cooled and quenched samples. This experiment suggests that upon annealing at 350°C, PEK crystallites undergo crystal perfection while the PEEK crystallites melt and are not able to recrystallize. The PEEK component of the blend appears to crystallize very poorly also on cooling compared to the pure PEEK polymer (compare curves B and A in *Figure 6*) or to the blend cooled from the melt (curve C in *Figure 2c*).

A possible cause of the observed behaviour of the blend is that well formed crystallites of PEK may reduce the mobility of the system, thereby hindering PEEK crystallization. This influence of the PEK crystallites on the crystallization of PEEK and the evidence of a slight melting point depression for the 50/50 wt% blend as shown by curve B of *Figure 6* suggests miscibility of the PEEK and PEK polymer in the amorphous state.

### *Amorphous phase*

The measurement of the glass transition temperature ($T_g$) is the most widely used test for miscibility of two polymers. The limitations of the use of glass transition temperatures as a criterion for blend miscibility and the methods of $T_g$ measurement in polymer blends have been reviewed by MacKnight *et al.*[15]

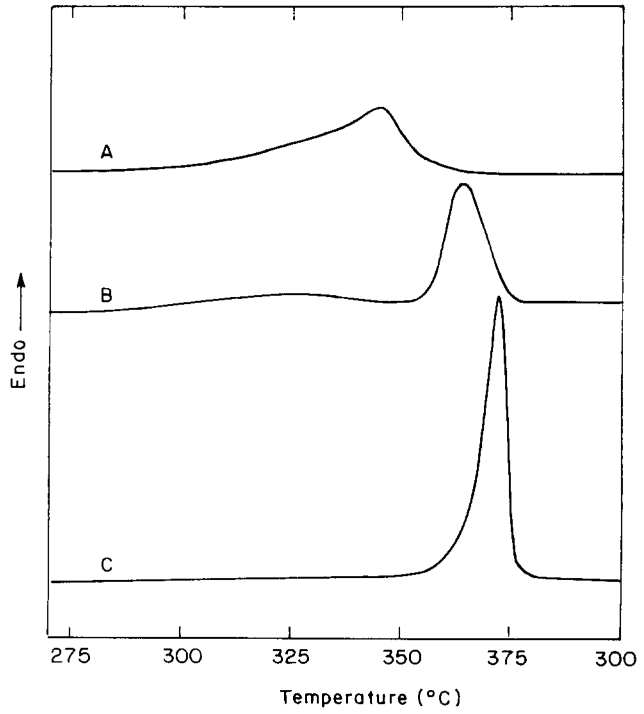

**Figure 6** D.s.c. melting scans of samples annealed at 350°C for 2 h and then cooled to room temperature at 1°C min$^{-1}$: A, PEEK; B, 50/50 blend; C, PEK

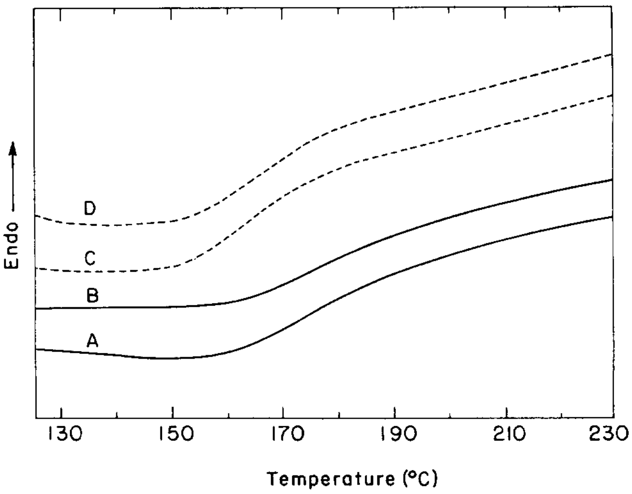

**Figure 7** D.s.c. scans in the glass transition region for precipitated powders heated at 25°C min$^{-1}$ up to the temperature $T_a$, and immediately cooled to room temperature (cooling rate of 1°C min$^{-1}$): A, 50/50 blend, $T_a = 250°C$; B, 50/50 physical mixture, $T_a = 250°C$; C, 50/50 blend, $T_a = 350°C$; D, 50/50 physical mixture, $T_a = 350°C$

It is difficult to detect the glass transition temperatures of the powders precipitated from solutions of dichloroacetic acid because of the interference by further crystallization which occurs immediately above the glass transition. The glass transition temperatures of the blends and of the pure polymers can instead be readily measured after annealing of the samples at any temperature in the range 250–400°C. PEEK/PEK blends of any compositions show a single glass transition temperature; however, the difference in the $T_g$ values of the two pure polymers is only 10°C and thus not resolvable by the commonly used techniques for the detection of $T_g$. In fact, the same single glass transitions as the coprecipitated materials were measured for the macroscopic physical mixture of the polymers, as shown in the d.s.c. scans of the samples after annealing at any temperature in the range 250–400°C (*Figure 7*).

## CONCLUSION

This study shows that separate crystalline phases are formed not only in PEEK/PEK blends close to thermodynamic equilibrium (isothermally crystallized, annealed at high temperature) but also in samples possibly far from equilibrium (cooled from the melt, precipitated from solution). However, cocrystallization seems to occur in this system upon rapid quenching of blends from the melt, as shown by the single composition dependent melting endotherms obtained upon quenching.

The presence of a single glass transition for macroscopic physical mixtures of the two polymers indicates that any conclusion about the miscibility in this system based on d.s.c. analysis is unjustified. However, the possible occurrence of cocrystallization on quenching allows one to infer that the two polymers are miscible in the melt state. The influence of well formed crystallites of PEK on the crystallization of PEEK in the blend, and the slight melting point depression observed for PEK crystals lends further support to this conclusion.

## ACKNOWLEDGEMENTS

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